

**Coöxidation of Benzaldehyde and Methyl Oleate.**—A solution consisting of 106 g. (1.0 mole) of benzaldehyde, 30 g. (0.1 mole) of 95% methyl oleate (containing 4% of saturated esters and 1% of methyl linoleate) and 180 ml. of acetone was coöxidized at 23–26° for twenty hours with dry air while the solution was being irradiated with ultraviolet light, as described previously.<sup>3</sup> It was not feasible to continue the coöxidation for more than twenty hours because of crystallization of benzoic acid in the fritted discs. The acetone solution was then cooled to –60° and the white precipitate which formed was filtered and freed of acetone. The product, which was a liquid at room temperature, was washed with 10% aqueous sodium bicarbonate, then with water, and finally dried over anhydrous calcium sulfate and filtered. The residual oil weighed 13.3 g. (42% yield) and consisted mainly of methyl 9,10-epoxystearate. Calcd. for oxirane oxygen, 5.09; sapon. equiv., 312.5. Found: oxirane oxygen, 4.33%; sapon. equiv., 311.3.

**Coöxidation of Benzaldehyde and Oleyl Alcohol.**—Repetition of the above experiment with 26.8 g. (0.1 mole) of 99% oleyl alcohol instead of methyl oleate, and crystallization of the reaction mixture at –65°, yielded 52 g. of crude product (acid number 241). This was washed acid-free with 6 *N* aqueous sodium hydroxide. The alkali-insoluble portion was a mushy solid (19 g.) having an oxirane oxygen content of 3.45% (calcd. 5.63). Recrystallization from ethyl acetate and then diethyl ether yielded 6 g. (21% yield) of impure 9,10-epoxyoctadecanol, m. p. 42–55° (lit.<sup>2</sup> 54°), and oxirane oxygen, 4.66%.

The aqueous, alkaline solution was acidified while hot, filtered, and cooled to room temperature, yielding 14 g. of benzoic acid, m. p. 122°.

**Coöxidation of Acetaldehyde and Oleic Acid.**—Twenty-eight grams (0.1 mole) of oleic acid, 44 g. (1.0 mole) of acetaldehyde and 240 ml. of acetone were coöxidized at 0–5° for twenty-four hours while the solution was irradiated with ultraviolet light.<sup>2</sup> The reaction solution was washed several times with water, and the residual oil was recrystallized from acetone at –25° yielding 4 g. (13% yield) of 9,10-epoxystearic acid, m. p. 50–52° (lit.,<sup>2</sup> 59°). Oxirane oxygen: calcd., 5.36; found, 4.59. Neutralization equivalent: calcd., 298.5; found, 292.5. Approximately 1/2 mole of acetic acid was formed during coöxidation.

**Coöxidation of Butyraldehyde and Oleic Acid.**—Twenty-eight grams (0.1 mole) of oleic acid, 72 g. (1.0 mole) of butyraldehyde and 195 ml. of acetone were coöxidized for 24 hours at 5° while the solution was irradiated with ultraviolet light.<sup>2</sup> The reaction mixture was worked up as described in the preceding experiment, yielding 6 g. (20% yield) of 9,10-epoxystearic acid, m. p. 50–53°. Oxirane oxygen, 4.56; neutralization equivalent, 299.2. Approximately 2/3 mole of butyric acid was formed during coöxidation. When the reaction was conducted at 30–50°, substantially the same yield of 9,10-epoxystearic acid but larger quantities of butyric acid were obtained. In the absence of ultraviolet radiation only about 1 g. of 9,10-epoxystearic acid was isolated.

EASTERN REGIONAL RESEARCH LABORATORY<sup>7</sup>  
PHILADELPHIA 18, PA.

RECEIVED MARCH 6, 1950

(6) Swern, Findley, Biffen and Scanlan, *Anal. Chem.*, **19**, 444 (1947).

(7) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

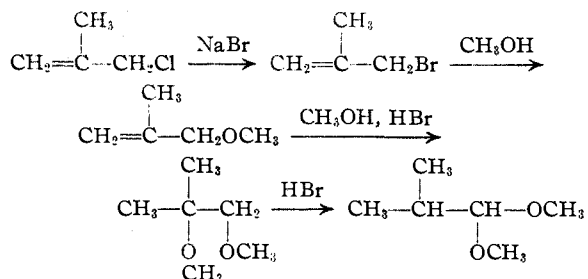
## Solvolysis and Rearrangement Reactions Accompanying the Formation of Methallyl Bromide

By P. TRUSCHER\*

In carrying out the preparation of methallyl bromide by reaction of methallyl chloride with sodium bromide in methanol, according to the

\* Deceased June 10, 1950.

method of Nichols, *et al.*,<sup>1</sup> the following additional products were isolated: methyl methallyl ether, 1,2-dimethoxy-2-methylpropane (isobutylene glycol dimethyl ether) and isobutyraldehyde dimethylacetal. Various observations were made which show that these products probably are formed in the order named, in a sequence of consecutive reactions, beginning with the conversion of methallyl chloride to methallyl bromide, as shown in the chart.



The pertinent experimental observations are the following: (1) The concentration of methallyl bromide passes through a maximum. At three hours reaction time, the yield of methallyl bromide was 37%, at eighteen hours 25%, and at twenty-two hours none was isolated. (2) It was shown by comparative experiments, in which the rates were followed by titration of the acid liberated, that the solvolysis of methallyl bromide in methanol occurs about one hundred times more rapidly than the solvolysis of methallyl chloride. The latter reaction, as an alternate path to methyl methallyl ether, is thus excluded and, in effect, sodium bromide is a catalyst for the etherification of methallyl chloride.

(3) The concentration of methyl methallyl ether could not be followed conveniently because of the troublesome methanol azeotrope. At eighteen hours reaction time, the yield of this product was approximately 10%. However, the appearance of this product must coincide with the development of free hydrogen bromide which becomes appreciable in about two hours and is most rapid at 3–3.5 hours.

(4) The yield of 1,2-dimethoxy-2-methylpropane and of isobutyraldehyde dimethylacetal at three hours is negligible; at eighteen hours the yield of the two products together, but with the former predominating, was 15%. Under more drastic conditions, the latter is reported to be the main product.<sup>2</sup>

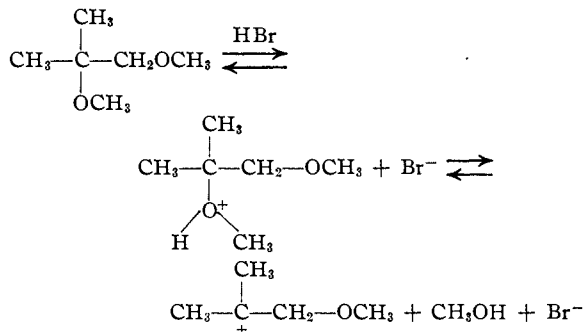
(5) Methyl methallyl ether, on refluxing with methanolic hydrogen bromide, was converted to a mixture of the glycol ether and the acetal. The acid catalyzed addition of methanol to methyl methallyl ether is a known type of reaction, as applied to isobutylene and other olefins.<sup>3</sup>

(1) Nichols, Wrigley and Yanovski, *THIS JOURNAL*, **68**, 2020 (1946).

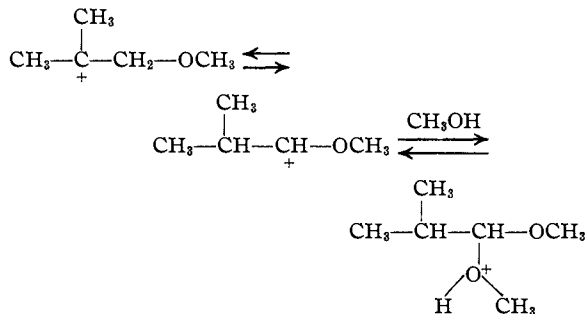
(2) Schmerling and Ipatieff, U. S. Patent 2,412,012; *C. A.*, **41**, 2070 (1947).

(3) Evans and Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).

(6) Similarly, 1,2-dimethoxy-2-methylpropane is converted in part to isobutyraldehyde dimethylacetal on refluxing with methanolic hydrogen bromide. This rearrangement has not been reported previously, but is not unexpected in view of the proposed mechanism for acid cleavage of ethers,<sup>4</sup> in this case



The cation would be expected to take part in a normal 1,2-rearrangement.



This mechanism suggests that the rearrangement of a given glycol ether would be most rapid when catalyzed by the acid most effective in cleaving ethers, *i. e.*, hydroiodic > hydrobromic > hydrochloric acids. Also, for a given acid catalyst, the rearrangement would be most rapid with the ethers most easily cleaved, *i. e.*, tertiary > secondary > primary ethers. Not enough data are available to test this.

From the standpoint of a practical method for the preparation of methallyl bromide, the foregoing observations suggest that a shorter period of reaction than the ten hours taken by Nichols, *et al.*,<sup>1</sup> would be advantageous, but at best the yield is rather unsatisfactory.

As expected, the solvolysis reaction of methallyl bromide in isopropyl alcohol was found to be slow; nevertheless, methallyl bromide was obtained from the chloride in only 34% yield upon refluxing with calcium bromide in isopropyl alcohol for three hours. In acetone, using lithium bromide and refluxing for four hours, methallyl bromide was formed to the extent of 40%. These results suggested that a limitation in yield may be imposed by reversibility of the reaction. This was confirmed by the isolation of methallyl chloride (35%) from a mixture containing originally only

lithium chloride and methallyl bromide in acetone.

#### Experimental

**1,2-Dimethoxy-2-methylpropane.**—The procedure of Nichols, *et al.*,<sup>1</sup> for the preparation of methallyl bromide was followed. The greater part of the methanol was removed by washing with water and the oil layer was dried and fractionated through a 28-inch tantalum wire spiral column. Twenty-two grams of methanol-methyl methallyl ether azeotrope, b. p. 60–64°, 35 g. of methallyl chloride, b. p. 70–75°, 100 g. of methallyl bromide, b. p. 92–94°, and 28 g. of a mixture, b. p. 107–115°, of isobutyraldehyde dimethylacetal and 1,2-dimethoxy-2-methylpropane were obtained from 270 g. of methallyl chloride. The last fraction was refractionated at a higher reflux ratio and the fraction, b. p. 110.0–110.5°, was stirred with silver nitrate solution for several hours to remove unidentified halogenated impurities which were not separated by fractionation. Redistillation yielded a liquid, b. p. 110.9° (752 mm.),  $n_D^{20}$  1.3952,  $d_4^{20}$  0.8559; calcd. for dimethoxymethylpropane: molar refraction 33.08. Found: molar refraction 32.96. *Anal.* Calcd. for  $\text{C}_6\text{H}_{14}\text{O}_2$ : C, 61.0; H, 11.86; methoxyl, 52.6. Found: C, 60.7; H, 11.9; methoxyl, 50.5.

The identity of this compound was established by the analysis, the non-identity with known isomers, and by the observation that isobutyraldehyde, isolated as the 2,4-dinitrophenylhydrazone, was formed when the compound was boiled with aqueous hydrochloric acid. The compound does not react with 2,4-dinitrophenylhydrazine acidified with sulfuric acid, even on boiling for ten minutes. The reaction, in the presence of hydrochloric or hydrobromic acid is rapid; on boiling, a precipitate of isobutyraldehyde dinitrophenylhydrazone forms within thirty seconds. In contrast, isobutyraldehyde dimethylacetal gives an immediate precipitate of the dinitrophenylhydrazone with 2,4-dinitrophenylhydrazine, acidified with sulfuric acid, in the cold.

**Reaction of Methyl Methallyl Ether with Methanol and Hydrobromic Acid.**—A mixture of 50 g. of methyl methallyl ether, 20 g. of 40% aqueous hydrobromic acid and 250 ml. of 99% methanol was refluxed for eighteen hours, washed with water, dried and fractionated, yielding 11 g. of a mixture, b. p. 110–115°, of isobutyraldehyde dimethylacetal and 1,2-dimethoxy-2-methylpropane.

**Rearrangement of 1,2-Dimethoxy-2-methylpropane by Anhydrous Methanolic Hydrobromic Acid.**—One ml. of pure 1,2-dimethoxy-2-methylpropane, free from acetal, was refluxed for a half-hour with 4 ml. of about 2 molar methanolic hydrogen bromide. After this time, the mixture smelled strongly of isobutyraldehyde dimethylacetal. With 2,4-dinitrophenylhydrazine, acidified with sulfuric acid, it formed an immediate precipitate, which was shown to be isobutyraldehyde 2,4-dinitrophenylhydrazone by mixed melting point.

**Reaction of Methallyl Chloride with Lithium Bromide in Acetone.**—One mole (90 g.) of methallyl chloride was refluxed with a solution of 1.2 moles (104.2 g.) of Kahlbaum lithium bromide (dried at 110° for twelve hours) in 250 ml. of acetone for four hours. The mixture consisted of two liquid phases throughout this period, and lithium chloride precipitated as the reaction proceeded. The acetone was removed by washing with water, and the oil layer was dried and fractionated yielding 54 g., b. p. 92–94° or 40% yield of methallyl bromide. This is a considerable improvement over the method of Tamele, *et al.*,<sup>5</sup> which uses sodium bromide in acetone and results in a 15–20% yield of methallyl bromide. The method of Nichols, *et al.*,<sup>1</sup> is the most practical method of forming methallyl bromide from the chloride, if a reaction time of three hours is used rather than the recommended ten.

**Reversibility of Methallyl Bromide Formation.**—Half a mole (67.5 g.) of methallyl bromide was refluxed for two days with one mole (32.5 g.) of lithium chloride. The

(4) A. E. Remick, *J. Org. Chem.*, **7**, 543 (1942).

(5) Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

mixture became brown during this time. Acetone was removed by washing with water, and the oil layer was dried and fractionated, yielding 16 g. (35.6%) of methallyl chloride, b. p. 72–75°, and 22.5 g. (32%) of methallyl bromide, b. p. 92–95°.

GEORGE HERBERT JONES LABORATORY  
UNIVERSITY OF CHICAGO  
CHICAGO 37, ILLINOIS

RECEIVED MARCH 22, 1950

## Derivatives of 1,2,3,4,5,6,7,8-Octahydroanthracene

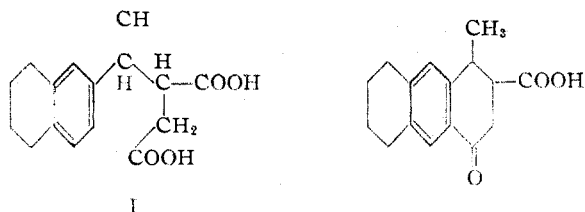
By D. L. TURNER

It was hoped that 2-carboxy-4-keto-1-methyl-1,2,3,4,5,6,7,8-octahydrophenanthrene<sup>1</sup> could be prepared utilizing the Stobbe condensation.<sup>2,3,4</sup>

Hydrogenation of the Stobbe half-ester from 2-acetylnaphthalene using Adams catalyst in acetic acid gave a mixture containing a small quantity of I. An additional quantity of I was obtained from the mother liquor from the catalytic hydrogenation by the Raney alloy procedure,<sup>5</sup> which has been used for the reduction of naphthalene compounds.<sup>6</sup>

The Stobbe condensation with 2-acetyl-5,6,7,8-tetrahydronaphthalene gave a mixture of half-esters, which was hydrolyzed with barium hydroxide to a crystalline unsaturated acid; this was reduced by the Raney alloy procedure to the same acid obtained from 2-acetylnaphthalene.

The acid (I) underwent cyclization to give 2-carboxy-4-keto-1-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (II). The carbonyl group was easily reduced to methylene, using hydrogen in the presence of palladium and perchloric acid.<sup>7</sup> The ultraviolet absorption spectrum of II is very similar to that of  $\alpha$ -tetralone,<sup>8,9</sup> with a bathochromic shift. The direction of ring-closure was shown by dehydrogenation to 1-methylanthracene.



### Experimenta

**3-Carboxy-4-(5,6,7,8-tetrahydro-2-naphthyl)-3(?)-pentenoic Acid.**—The Stobbe condensation of 310 g. of

(1) An hypothesis to be described elsewhere suggests that this substance might exhibit the biological activity of myelokentric acid.

(2) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 636 (1935).

(3) J. W. Cook and A. M. Robinson, *ibid.*, 505 (1938).

(4) W. S. Johnson, A. Goldman and W. P. Schneider, *THIS JOURNAL*, **67**, 1357 (1945).

(5) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

(6) D. Papa, E. Schwenk and H. Breiger, *ibid.*, **14**, 366 (1949).

(7) K. W. Rosenmund and E. Karg, *Ber.*, **75**, 1850 (1942).

(8) P. Ramart Lucas and M. J. Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935).

(9) D. Biquard, *ibid.*, **8**, 55 (1941).

2-acetyl-5,6,7,8-tetrahydronaphthalene with 380 g. of dimethyl succinate in the presence of potassium *t*-butoxide (from 80 g. of potassium and 1600 ml. of *t*-butyl alcohol) was carried out by the method of Johnson, Goldman and Schneider.<sup>4</sup> This gave 390 g. of liquid half-esters.

Part of the product (40 g.) was dissolved in 230 ml. of 95% ethanol. To this was added 87 g. of barium hydroxide octahydrate and 250 ml. of water. After refluxing for 1.5 hours, the mixture was cooled and filtered. The barium salt was decomposed with dilute hydrochloric acid and the product was taken up in ether. Evaporation of the ether gave 20 g. of crystalline acid, m. p. 176–184°. This was recrystallized from acetic acid and ethyl acetate, m. p. 184–186° (dec.).

*Anal.* Calcd. for  $C_{16}H_{18}O_4$ : C, 70.05; H, 6.61. Found: C, 69.96; H, 6.60.

**3-Carboxy-4-(5,6,7,8-tetrahydro-2-naphthyl)-valeric Acid.**—(a) The Stobbe half-esters (25 g.) from 2-acetylnaphthalene, prepared by the potassium *t*-butoxide catalyzed reaction<sup>4</sup> using dimethyl succinate, were dissolved in 200 ml. of acetic acid and hydrogenated over 2.0 g. of Adams catalyst starting at 3 atmospheres pressure in a Burgess-Parr hydrogenation apparatus. When the uptake of hydrogen ceased, the catalyst was filtered and the solution was distilled *in vacuo*. The residual oil was hydrolyzed by refluxing for two hours with 100 ml. of ethanol and 45 ml. of 45% potassium hydroxide. Then 100 ml. of water was added and the ethanol was removed by distillation *in vacuo*. The solution was cooled, acidified and extracted with ether. The ethereal solution was dried and distilled and the product crystallized from chloroform; it was not homogeneous. Crystallization from acetone gave 2 g., m. p. 191–194° (dec.). The acetone mother liquor was evaporated and the crystalline residue (13 g.) was dissolved in 350 ml. of 10% sodium hydroxide and reduced with 40 g. of Raney nickel-aluminum alloy.<sup>5</sup> This procedure gave a crystalline product, which, after recrystallization from chloroform, weighed 9 g.; m. p. 193–194° (dec.). There was no depression in m. p. when mixed with the preceding product. A sample sublimed *in vacuo* and crystallized from ether-pentane had m. p. 195–196° (gas evolution).

*Anal.* Calcd. for  $C_{16}H_{20}O_4$ : C, 69.54; H, 7.30. Found: C, 69.24; H, 7.24.

(b) The pentenoic acid (30 g.) from 2-acetyltetralin was reduced by the Raney alloy procedure in 1250 ml. of 10% sodium hydroxide using 140 g. of Raney alloy. The crystalline product, m. p. 178–184°, weighed 20 g. A sample was crystallized several times from ethyl acetate and chloroform, m. p. 193–194° alone or when mixed with the acid described in (a).

**4-Keto-1-methyl-1,2,3,4,5,6,7,8-octahydroanthracene-2-carboxylic Acid.**—The preceding acid (17.5 g.) was refluxed with 150 ml. of acetyl chloride for two hours. The acetyl chloride was distilled but the resulting oil could not be crystallized. This anhydride was added slowly to a stirred solution of 19.8 g. of aluminum chloride in 100 ml. of nitrobenzene which was cooled to keep the temperature below 10°. The mixture was allowed to come to room temperature and after standing overnight it was hydrolyzed with ice and hydrochloric acid and steam distilled to remove nitrobenzene. The residue was taken up in ether and acids were taken out with 5% sodium carbonate. This solution was acidified and extracted with ether. Evaporation of the ether gave a gum which crystallized from nitromethane, m. p. 184–189°; weight 8 g. It was recrystallized from ether-pentane, m. p. 192–193°.

*Anal.* Calcd. for  $C_{16}H_{18}O_3$ : C, 74.40; H, 7.02. Found: C, 74.57; H, 6.98.

The ultraviolet absorption spectrum determined with the Beckman spectrophotometer, model DU,<sup>1</sup> was taken using solutions of the acid in 95% ethanol and showed maxima at 265  $m\mu$  ( $\log \epsilon$  4.19) and 304  $m\mu$  ( $\log \epsilon$  3.42) and minima at 235  $m\mu$  ( $\log \epsilon$  3.35) and 294  $m\mu$  ( $\log \epsilon$  3.33). The shape of the curve was similar to that for  $\alpha$ -tetralone,<sup>8,9</sup> with very broad bands.